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by

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EXPERIMENTAL AND THEORETICAL STUDIES IN PLANETARY AERONOMY

Quarterly Progress Report

Covering the Period 1 October 1965
through 31 December 1965

Prepared under Contract No. NASW-1283

TABLE OF CONTENTS

I. INTRODUCTION

This is the Third Quarterly Progress Report which describes the technical progress from 1 October 1965 through 31 December 1965 under NASA Contract No. NASW-1283. Scientific investigations accomplished during the current reporting period resulted in the generation of the following papers submitted and/or accepted for publication in accredited scientific journals, books and/or GCA Technical Reports or presented at scientific meetings.

Technical Papers Submitted and/or Accepted for Publication

	Publication
a. Submitted	
CO_2 Actinometer for Argon Source (P. Warneck)	J. Opt. Soc. Am.
Gas Analysis by Photoionization Mass Spectrometry (W. Poschenrieder and P. Warneck)	J. Applied Phys.
Ionization Potential of O_2 (J.A.R. Samson and R. B. Cairns)	J. Opt. Soc. Am.
Total Absorption Cross Sections of CO and CO_2 in the Region 550-200Å (R. B. Cairns and J.A.R. Samson)	J. Opt. Soc. Am.
Photon Scattering Cross Sections at Lyman-Alpha (1215.7Å) for He, Ne, A, H_2 and N_2 (F. F. Marmo, Shardanand and Y. Mikawa)	The Phys. Review
b. Accepted	
Total Absorption Cross Section of Atomic Oxygen Below 910Å (R. B. Cairns and J.A.R. Samson)	The Phys. Review 139, A1403-A1407 (1965)

Published GCA Technical Reports

	GCA TR No.
PHYSICS OF PLANETARY ATMOSPHERES IV: Gas Analysis by Photoionization Mass Spectrometry (W. Poschenrieder and P. Warneck)	66-1-N
PHYSICS OF PLANETARY ATMOSPHERES V: Ionization Potential of O_2 (J.A.R. Samson and R. B. Cairns)	65-30-N

Technical Papers Presented at Scientific or Professional Meetings

VUV Reflectivity from a Solar-Illuminated Earth Atmosphere (F. F. Marmo and T. C. Degges) — INVITED PAPER presented by F. F. Marmo at International Symposium on Electromagnetic Sensing of the Earth from Satellites held in Miami, Florida, on November 22-24, 1965, who also attended the Second AAS Symposium on Interactions of Space Vehicles with an Ionized Atmosphere held in Miami, Florida, on November 26-27, 1965.

In Section II, technical summaries are given on the work performed under the present contract. During the current reporting period, significant progress has been achieved in the following areas:

A. Photochemistry of planetary atmospheres

B. Laboratory investigations in the VUV and EUV spectral regions

C. Planetary aeronomy

D. Collateral investigations.

II. TECHNICAL SUMMARIES OF WORK PERFORMED DURING THIS QUARTER

A. PHOTOCHEMISTRY OF PLANETARY ATMOSPHERES

1. The Role of $O(^1D)$ in Reactions with O_3

In this work phase the photolysis of oxygen at 1470Å is utilized to produce $O(^1D)$ simultaneously with $O(^3P)$, and the production of ozone is investigated as a function of several parameters. Work was begun in the last Quarter and continued through the present reporting period. The influence upon the ozone quantum yield of several important experimental parameters has now been investigated in detail so that they are not repeated here.

The experimental details are given in GCA Technical Report No. 64-7-N. The parameters investigated are: pressure, temperature, flow rate (at atmospheric pressure) and rare gas admixture. Sufficient experimental data have now been obtained for some forthcoming analysis concerning pressure and temperature dependence. In Figs. 1 through 3 are shown experimentally-determined ozone quantum yields as a function of pressure for three different temperatures. It can be seen that in all three cases the amount of ozone formation decreases with decreasing pressure. These results thus verify the preliminary data discussed in the previous Quarterly Progress Report. However, in the present work considerable care was exercised to keep the light intensity and the flow rates constant while varying the pressure. Also, the pressure in the reactor was measured with an accurate mechanical gauge rather than with a mercury manometer as previously to avoid the perturbing presence of mercury. Thus, considerable confidence can be placed upon the new final data.

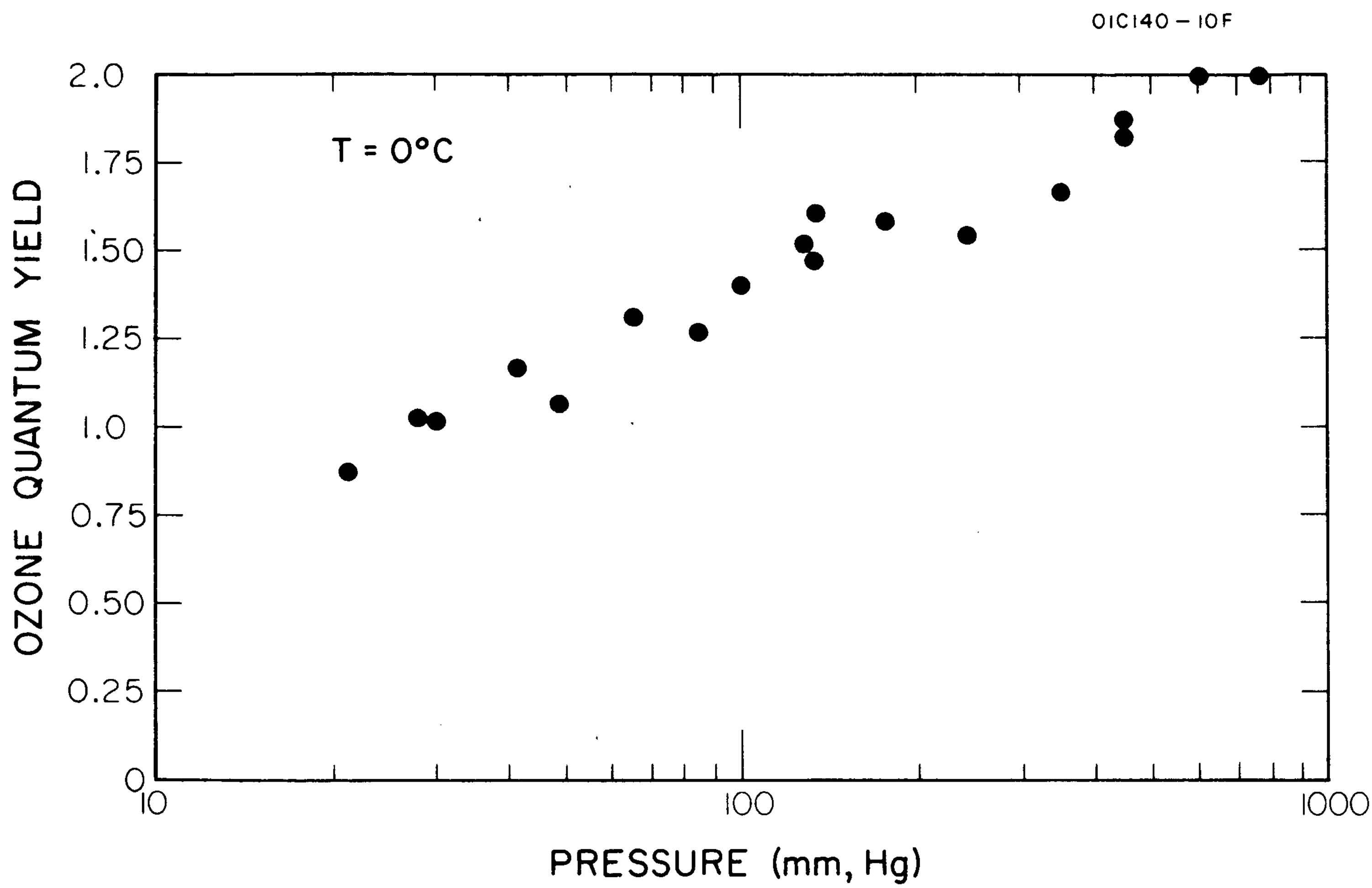
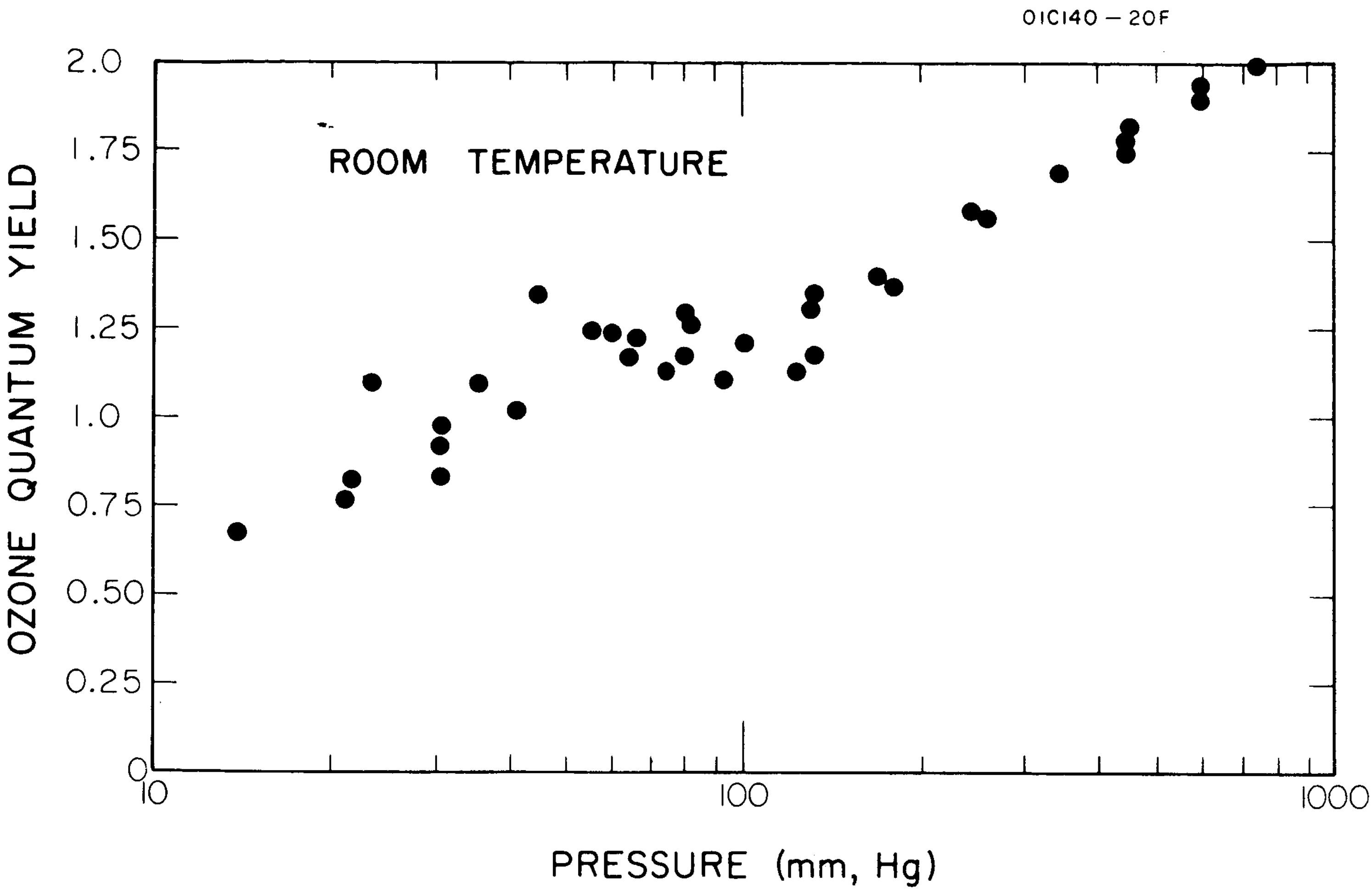

01C140 - 10F
T = 0°C
OZONE QUANTUM YIELD
2.0
1.75
1.50
1.25
1.0
0.75
0.50
0.25
0
10
100
1000
PRESSURE (mm, Hg)

Figure 1.



01C140 — 20F
ROOM TEMPERATURE
OZONE QUANTUM YIELD
PRESSURE (mm, Hg)
2.0
1.75
1.50
1.25
1.0
0.75
0.50
0.25
0
10
100
1000

Figure 2.

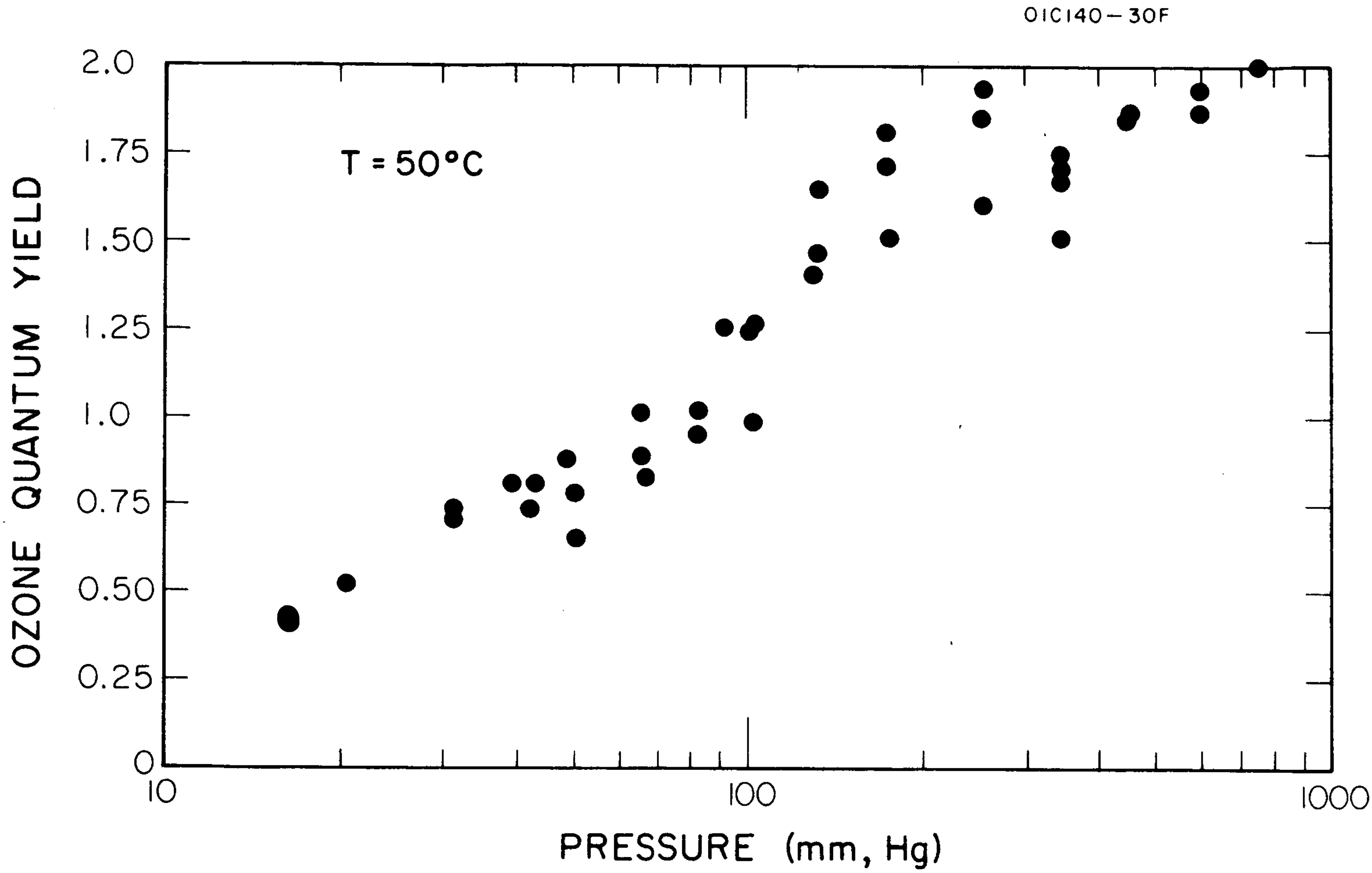

OIC140—30F
2.0
1.75
1.50
1.25
1.0
0.75
0.50
0.25
0
OZONE QUANTUM YIELD
T = 50°C
10
100
1000
PRESSURE (mm, Hg)

Figure 3.

However, a thorough analysis has as yet not been performed so that information on the detailed reaction mechanism and rate constants must await this effort. Further experiments, currently in progress, will give additional data on rare gas admixture to determine third-body activity, and data on admixture of nitrogen to provide additional information of the $O(^1D)$ deactivation rate.

2. Role of Minor Constituents in Planetary Atmospheres

Concerning the role of minor constituents in planetary atmospheres the following comments are pertinent. It appears that it is especially timely to investigate VUV photolysis of minor constituents in simulated planetary atmospheres in order to resolve some current problems associated with the interpretation of spectra of the atmospheres of Mars and Venus. Specifically, during a recent meeting (Symposium on Electromagnetic Sensing) held in Miami, Florida, on November 22-24, 1965, F. F. Marmo discussed some of these problems with Dr. L. Kaplan of JPL who is currently attempting an analysis of planetary spectra. Dr. Kaplan made it clear that these spectra are unexpectedly complex in that they contain many features which are as yet unidentifiable due to the lack of pertinent laboratory data. It is his feeling that much of these spectra can be associated with organic compounds, radicals and other complex intermediates. It was mutually agreed that the importance of obtaining VUV photolysis data on simulated atmospheres is evident.

Initially, it is planned to include minor constituents such as water vapor, methane, ozone, nitrogen oxides, gaseous sulfur compounds and others. The photochemical studies will be performed on mixtures containing these constituents with oxygen and/or carbon dioxide. Since it would be of special value to detect intermediates and radicals, it is planned to employ appropriate experimental apparatus such as open ion sources, continuous monitoring MS, etc. Preliminary design of the appropriate apparatus suggests that the initial VUV photolysis experiments will be carried out in a 1-liter Pyrex flask joined to the continuous MS inlet. A hydrogen light source fitted with either barium or lithium fluoride windows would be employed initially. The gas sample or simulated atmosphere mixture will be contained in a 12-liter storage bulb and the flow would be controlled by an adjustable leak valve. The apparatus incorporating these features is currently being set up and will be completed within the forthcoming Quarter.

B. LABORATORY INVESTIGATIONS IN THE VUV (1000-2000Å) AND THE EUV (BELOW 1000Å)

1. The Mass Analysis of Photoionization Products

This portion of the program has been completed. The results have been published as GCA Technical Report No. 66-1-N entitled "PHYSICS OF PLANETARY ATMOSPHERES IV: Gas Analysis by Photoionization Mass Spectrometry" by W. Poschenrieder and P. Warneck. This material has also been submitted for publication in the Journal of Applied Physics. Only a very brief abstract of the work performed is given in this report since the details are available to the interested reader.

A unique mass spectrometer (MS) was designed, developed and constructed, which features a special 180-degree magnetic analyzer with inclined pole faces, in order to obtain the required high transmission factor. This instrument was coupled to a ½-meter Seya-type VUV monochromator which supplied the photoionizing source. The mass analysis of the photoionization products from several planetary gases has been performed in order to demonstrate some of the major advantages of this gas analytical technique. It is shown that this technique yields photon-molecule interaction data which are not obtainable by ordinary electron impact methods. Finally, it is demonstrated that with minor modifications, these MS-monochromator techniques can be applied to ion-molecule reaction studies with significant advantage over electron impact techniques.

2. Electron Energy Spectrum Due to EUV and VUV Photoionization

The spherical electron energy analyzer has been constructed and tested with undispersed radiation. However, the use of undispersed radiation proved to be unsuccessful due to the copious supply of helium metastable atoms from the light source. The metastable atoms produced electrons on collision with the metal walls. The signal from the metastables was several orders of magnitude greater than the photoionization signal. Since the ultimate aim of this program is to study the kinetic energies of the photoelectrons with monochromatic light, further effort to subdue the metastables is not being pursued. Instead, the apparatus is now attached to the exit slit of a ½-meter Seya monochromator. Preliminary tests have been made. No metastable current is detected in this arrangement; however, problems still exist which have tentatively been traced to a copious emission of photoelectrons. These electrons have a continuous range of kinetic energies which mask the structure expected from the electrons produced by photoionization.

Steps are being taken to prevent the vacuum ultraviolet radiation from striking any metal parts within the analyzing region. In this regard, Fig. 4 shows the new modified arrangement of a precision set of spheres including the new light defining tubes. The tubes are essential to confine the region of photoionization to the center of the spheres, thus improving resolution. However, great care must be taken to prevent the radiation from striking the tubes since the photoelectrons released mask the electron current from the gas. A further change from the previous analyzer is in constructing the entire sphere from open mesh in order to reduce the surface area from which secondary electrons can be released. The technical problems of producing self-supporting spheres from a mesh have now been overcome. A further reduction of surface area has been achieved by etching the spheres after construction. This new configuration is currently under test and appears to produce results which are superior to those obtained with the design described in the previous Quarterly Report.

3. Atomic Hydrogen Absorption Cross Section

At present, this project is receiving a considerable amount of attention. Apparatus has been constructed in which studies can be made of the relative efficiencies of production of atomic hydrogen by microwave or radio frequency discharges of varying frequencies and power levels.

A Wrede-Harteck gauge has been constructed for the measurement of the atomic hydrogen concentration.

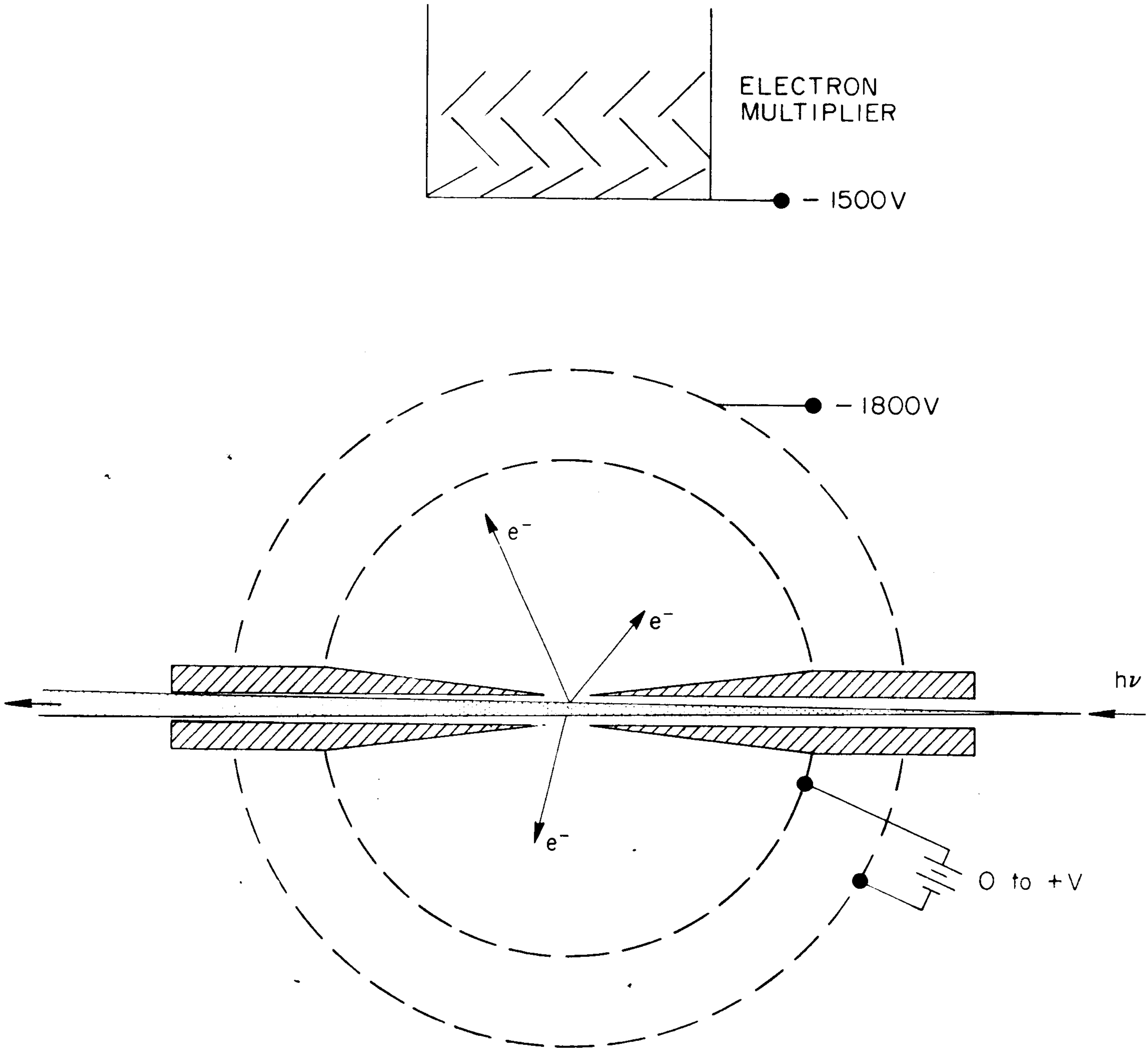


Figure 4.

The assembled apparatus has undergone routine vacuum testing and is, at present, being thoroughly outgassed and cleaned, a procedure necessary to inhibit wall recombination of the atomic species.

It is anticipated that within the next Quarter, the most suitable techniques for the production and measurement of atomic hydrogen will be available and that the absorption tube will be mounted onto the spectrograph giving preliminary quantitative data.

4. Variation of Photoionization Threshold with Temperature

One of the subtasks of the present program is to investigate the variation of the photoionization threshold with temperature in order to identify unambiguously that threshold for certain planetary gases. The capability and manner in which this technique has been employed is demonstrated in an investigation which resulted in the generation of GCA Technical Report No. 65-30-N entitled "PHYSICS OF PLANETARY ATMOSPHERES V: Ionization Potential of O_2" by J. A. R. Samson and R. B. Cairns. This material has been submitted for publication in the Journal of the Optical Society of America. Although no detailed account is given here, the comprehensive study deserves some discussion in that it illustrates a new procedure which is applicable to other important atmospheric molecules.

Initial experiments showed that the photoionization of oxygen ions appeared at about 1046Å which is approximately 20Å longer than previous measurements. The question arises, then, "Does this represent the true ionization threshold and if not, what is the nature of the ions being measured at these longer wavelengths?" The variation of the photoionization threshold with temperature was employed in order to evaluate the role of photoionization of vibrationally-excited molecules. It is this aspect of the investigation which was most important in establishing the absence of vibrationally-excited molecules so that additional experiments were indicated in order to establish the true ionization potential. Further investigations showed that the photoionization yield decreased with pressure and extrapolated to zero in a high vacuum. This ruled out a collisional process for the products of the long wavelength ions. To measure the true onset and to eliminate any pressure effects, a new low pressure (10^{-4} torr) ionization experiment was performed. Only then was the true ionization potential of O_2 established at 1027.8Å. Finally, comparison of these data with high-resolution photographic absorption data for oxygen involved the vibrational levels of the ion in such a manner as to unambiguously identify this threshold value. From the interpretation of the results, the dissociation energy for the ground state of the ion is 6.669 ± 0.001 eV and the electron affinity of O_2 is $\geq$ 0.21 eV.

5. Absorption and Photoionization Cross Sections

During this Quarter, the absorption cross sections were measured for CO and CO_2 in the wavelength region 550 to 200Å. The results of this investigation are included in a report entitled "Total Absorption Cross Sections of CO and CO_2 in the Region 550Å to 200Å" by R. B. Cairns and J. A. R. Samson which has been submitted to the Journal of the Optical Society of America for publication. Accordingly, only a very brief description of the results is given here.

Values of the total absorption cross sections of CO and CO_2 have been measured at wavelengths between 550 and 200Å as shown in Figure 5. The

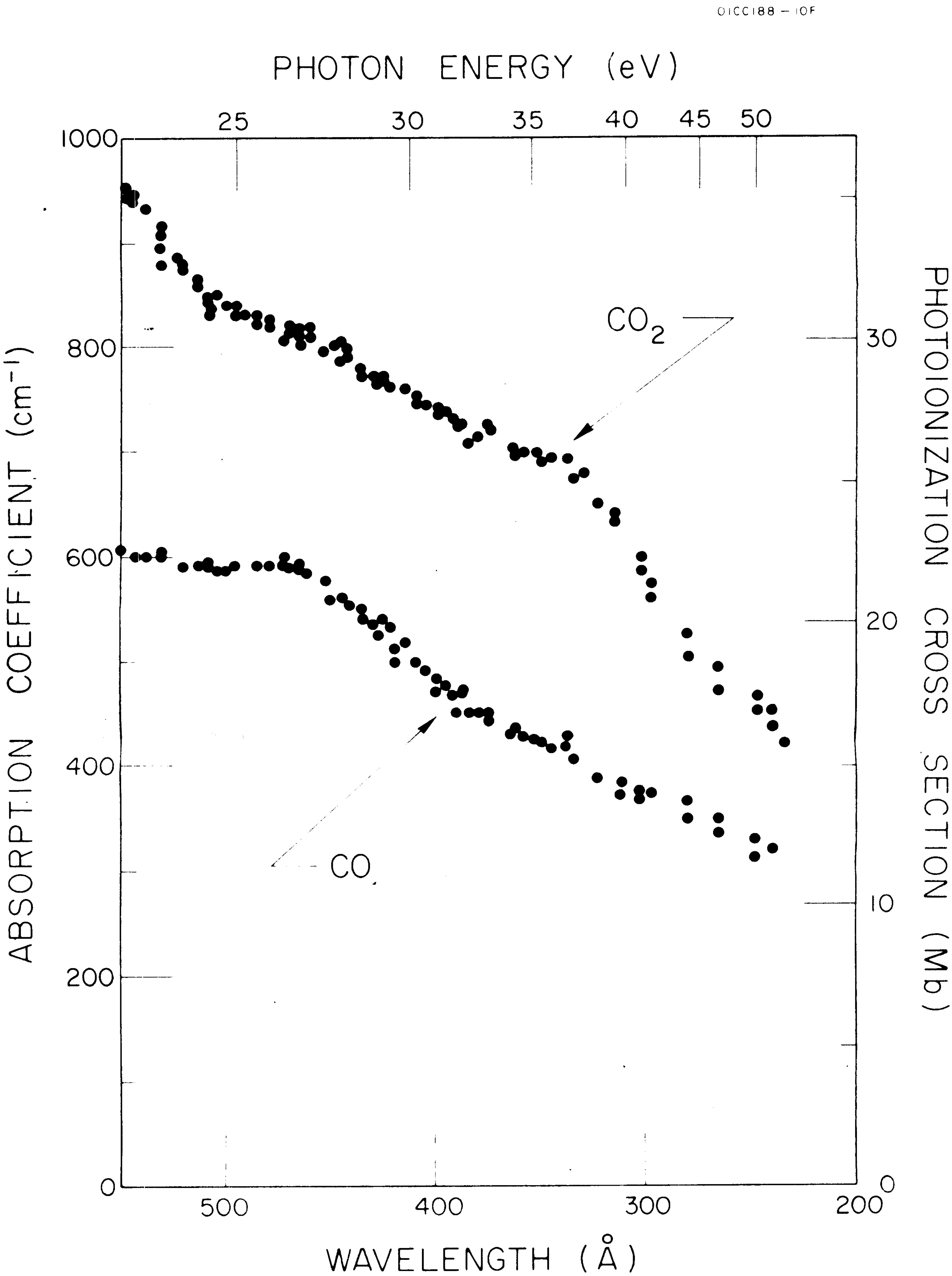

01CC188 – 10F
PHOTON ENERGY (eV)
25
30
35
40
45
50
1000
800
600
400
200
0
ABSORPTION COEFFICIENT (cm^{-1})
30
20
10
0
PHOTOIONIZATION CROSS SECTION (Mb)
CO_2
CO
500
400
300
200
WAVELENGTH (Å)

Figure 5.

experimental techniques employed and previously-described give only the total cross section and not the individual cross sections of the several contributing processes. It was found that the cross sections were independent of the pressure of the absorbing gas so that Beer's law obtains. There is good agreement with previously-reported measurements.

C. PLANETARY AERONOMY

1. Scattering Efficiency of Planetary Gases for Wavelengths Below 3000Å

The final measurements have been performed on the photon scattering cross sections at Lyman-alpha for He, Ne, A, H_2 and N_2. The results have been submitted for publication in The Physical Review in a paper entitled "Photon Scattering Cross Sections at Lyman-alpha (1215.7Å) for He, Ne, A, H_2 and N_2" by F. F. Marmo, Shardanand and Y. Mikawa.

Photon scattering cross-section measurements at Lyman-alpha have recently been reported by Gill and Heddle for the cases of A, H_2, N_2, Xe and Kr. These gases were investigated in the present experiment which employed a microwave-powered hydrogen light source with an oxygen filter to isolate the Lyman-alpha radiation and a highly-sensitive NO-filled Geiger counter. Additionally, for the first time, the low relative cross-section values of Ne and He were obtained. For the cases of A, H_2 and N_2, the relative scattering cross-section results compare favorably with those of Gill and Heddle whereas for the cases of Xe and Kr serious discrepancies were noted. Finally, Chan and Dalgarno have reported a theoretical value for He at Lyman-alpha of 3.5×10^{-26} cm^2 so that the present results could be placed on an absolute basis.

A laboratory study which represents a logical extension of the results discussed above was performed in which the pressure and temperature dependence of xenon was investigated to determine the role of molecular xenon. Most of the results of this investigation have been discussed in the previous Quarterly Report except for some new data which have been obtained during this Quarter. The interpretation of the over-all results has now been completed in the form of a scientific paper which is to be submitted for publication shortly.

These experiments employing undispersed radiation only at Lyman-alpha have made evident the need for the measurement of scattering cross sections at several wavelengths with dispersed radiation throughout the VUV region. For this purpose, it has been previously shown that an attenuation technique must be employed to obtain the new cross section data. An appropriate apparatus has been designed, constructed, checked out and found to be capable of yielding reliable results. The experimental procedure involves the attenuation measurements on selected gases including observation of the variation of temperature and pressure so that the role of molecular gases could also be uniquely evaluated. These measurements are essentially complete. A detailed description of the apparatus, the techniques and procedure employed is not appropriately given here since some recent modifications have been incorporated; in addition, this phase is best included in the discussion of results given in the next Quarterly Report.

2. Fluorescence Efficiency of Planetary Gases for Wavelengths Below 3000Å

VUV fluorescence due to electron bombardment of atmospheric gases was discussed in the previous Quarterly Report. In addition, a simple experiment was outlined in which to check some of the theoretical aspects. To date, no reliable experimental data have been obtained since some minor difficulties persist. An alternative laboratory technique for studying the VUV fluorescence of atmospheric gases is available by the generation of the nitrogen afterglow by microwave discharge. A laboratory investigation has been performed and interpreted in terms of a detailed mechanism due to Bayes and Kistiakowsky. On this basis, self-quenching cross sections were derived for the quenching of the Lyman-Birge-Hopfield (LBH) VUV bands of about 10^{-18} cm^2. This value can be applied to the study of atmospheric aurora. This phase is still incomplete so that a rather detailed account is given below.

The different characteristics of the Lewis-Rayleigh afterglow of nitrogen have been extensively reviewed.[1-3] Previously, only first positive bands ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$) were observed in its spectrum. The intensity distribution of these bands is striking, which indicates a favorable excitation of 12th, 11th and 6th vibrational levels of $B^3\Pi_g$ level. Later on, a new band system ($y^3\Sigma_u^- - B^3\Pi_g$) was also found[4-6] in the near infrared region of the spectrum of the Lewis-Rayleigh afterglow of N_2. In contrast with the above two band systems which lie in the visible and infrared regions, Tanaka, et al.[7] reported the presence of the weak LBH system ($a^1\Pi_g - x^1\Sigma_g^+$) in the vacuum ultraviolet region of the emission spectrum of the nitrogen afterglow.

Berkowitz, et al.[8] showed that the recombination of $N(^4S)$ atoms is responsible for the characteristic first positive bands emitted in the Lewis-Rayleigh afterglow of nitrogen. They further proposed that $^5\Sigma_g^+$ nitrogen molecules are in equilibrium with nitrogen atoms. On the basis of extensive observations of the bands of $B^3\Pi_g - A^3\Sigma_u^+$ and $y^3\Sigma_u^- - B^3\Pi_g$, Bayes and

Kistiakowsky[9-10] concluded that the emission of the above two band systems is mainly due to the collision-induced transition of nitrogen molecules from $^5\Sigma_g^+$ level to $B^3\Pi_g$ and $y^3\Sigma_u^-$ levels. A direct kinetic evidence for the elucidation of the excitation mechanism of LBH system in the afterglow of active nitrogen is not available. However, on the basis of the observed predissociation in the $a^1\Pi_g$ state of N_2, the above mechanism has also been assumed[7,10] for the excitation of the LBH system. The present study of the vacuum ultraviolet emission from the nitrogen afterglow provides direct evidence in favor of the above assumption and also provides information regarding the self-quenching of the N_2 $a^1\Pi_g$ state. The latter information is of interest for determining the optimum conditions of excitation of the LBH bands.

a. Experimental

The intensities of the visible and vacuum ultraviolet radiations emitted from the nitrogen afterglow were simultaneously measured under different conditions of the afterglow. The nitrogen afterglow was produced in a conventional fast flow system suitable for pressures up to about 1 mm Hg pressure and is shown in Figure 6. The afterglow was produced by the microwave discharge through the flowing nitrogen. The flow of nitrogen was controlled by a needle valve and measured by a capillary flow meter. The pressure in the afterglow tube was measured by means of a McLeod Gauge.

The intensity of the visible radiation (predominantly due to the first positive bands of N_2) from the nitrogen afterglow was measured with a 1P28 photomultiplier tube. The output of the photomultiplier was fed to the micro-microammeter. The vacuum ultraviolet radiation (LBH system is

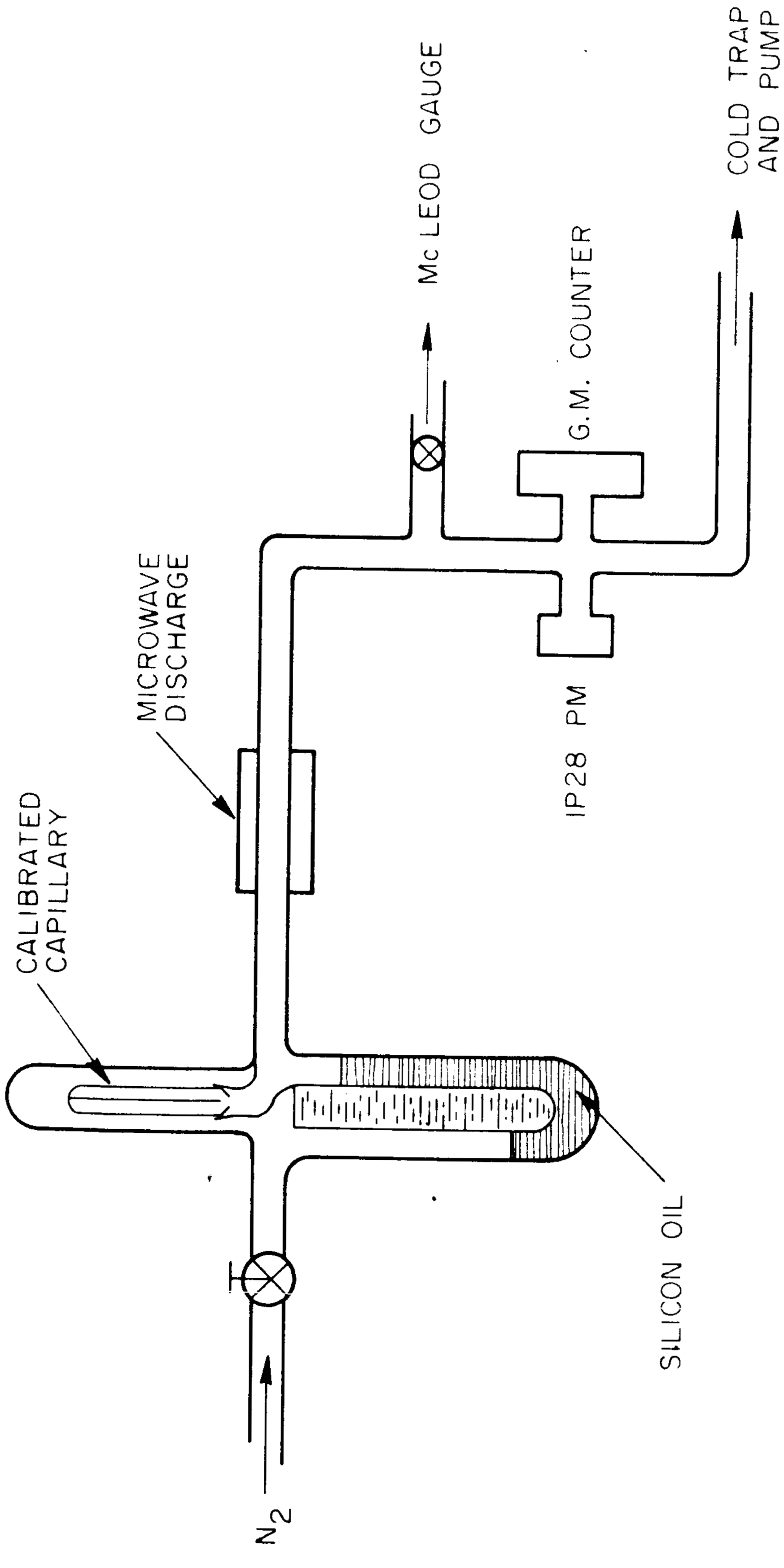
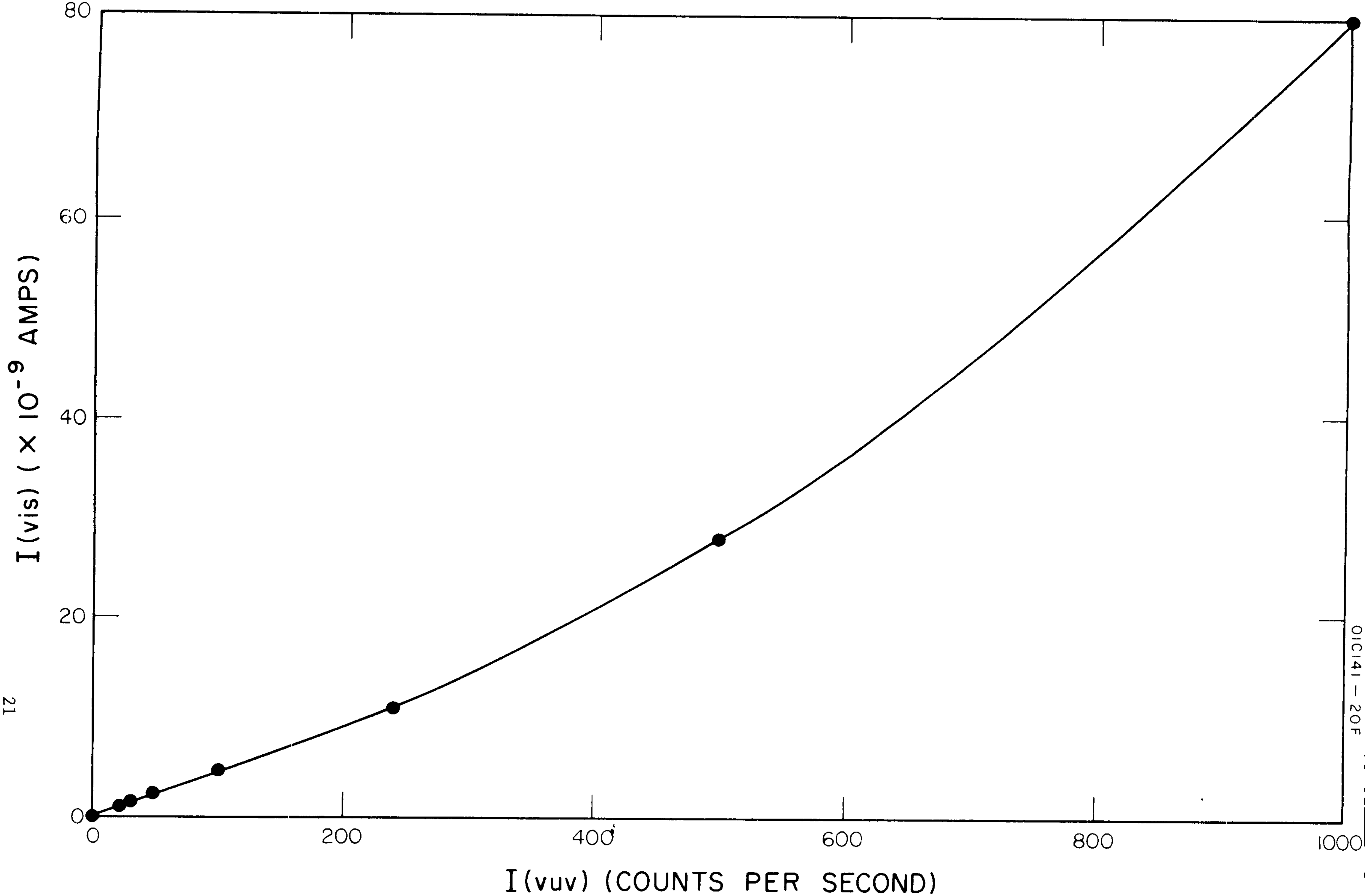

CALIBRATED CAPILLARY
MICROWAVE DISCHARGE
Mc LEOD GAUGE
G.M. COUNTER
COLD TRAP AND PUMP
IP28 PM
SILICON OIL
N_2

Figure 6.

the only emission observed[7] in the vacuum ultraviolet region) from the Lewis-Rayleigh afterglow of nitrogen was observed with a Geiger counter which was essentially of the type used by Chubb, et al.[11] and was used in conjunction with an oscilloscope. It was filled with 10 mm Hg of nitric oxide and is equipped with a lithium fluoride window affording a useful wavelength range of 1050Å to 1340Å. When operating between 570 and 590V, it was found that its response is linear to an accuracy of about 1 percent at 100 to 3000 counts per second; i.e., within the present range of observation.

The nitrogen flow rate was adjusted to obtain a suitable pressure in the afterglow tube and then the microwave discharge was initiated. The characteristic straw-yellow afterglow could be immediately observed in the tube. After allowing the system to reach equilibrium, the intensities of the visible and vacuum ultraviolet emissions from the Lewis-Rayleigh afterglow of nitrogen were recorded. Subsequently, the nitrogen pressure was varied and the above observations were repeated for several N_2 pressures. The observed intensity of the visible radiation is plotted against the intensity of vacuum ultraviolet radiation in Figure 7. It is apparent that the intensity of visible radiation is linearly related with that of the vacuum ultraviolet radiation at pressures below about 250 microns. At higher pressures, the relative intensity of the vacuum ultraviolet radiation with respect to that of the visible radiation decreases.

The effect of the introduction of nitric oxide after the discharge was also observed on the intensity of the visible and vacuum ultraviolet emission from the nitrogen afterglow. It was found that both emissions were quenched at about the same flow rate of nitric oxide.



OIC141 — 20F
I(vis) (× 10^-9 AMPS)
80
60
40
20
0
0
200
400
600
800
1000
I(vuv) (COUNTS PER SECOND)

Figure 7.

b. Discussion

The detailed mechanism of the excitation of various spectral features in the emission of Lewis-Rayleigh afterglow of nitrogen is given by Bayes and Kistiakowsky[10] and is as follows:

$$N(^4S) + N(^4S) + M \rightarrow N_2(^5\Sigma_g^+) + M \qquad k_1 \qquad (1)$$

$$N_2(^5\Sigma_g^+) + M \rightarrow N(^4S) + N(^4S) + M \qquad k_2 \qquad (2)$$

$$N_2(^5\Sigma_g^+) + M \rightarrow N_2(B^3\Pi_g) + M \qquad k_3 \qquad (3)$$

$$\rightarrow N_2(y^3\Sigma_u^-) + M \qquad k_4 \qquad (4)$$

$$\rightarrow N_2(^3\Delta_u) + M \qquad k_5 \qquad (5)$$

$$\rightarrow N_2(a^1\Pi_g) + M \qquad k_6 \qquad (6)$$

$$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu \qquad A_3 \qquad (7)$$

$$N_2(y^3\Sigma_u^-) \rightarrow N_2(B^3\Pi_g) + h\nu \qquad A_4 \qquad (8)$$

$$N_2(^3\Delta_u) \rightarrow N_2(B^3\Pi_g) + h\nu \qquad A_5 \qquad (9)$$

$$N_2(a^1\Pi_g) \rightarrow N_2(X^1\Sigma_g^+) + h\nu \qquad A_6 \qquad (10)$$

where k's are the rate coefficients and A's are the radiative transition probabilities. The radiative transition expressed in (9) is not observed because it lies in the far infrared. However, this process (9) is assumed[10] to explain the behavior of the first positive bands emitted from $B^3\Pi_g$ ($V' = 7, 6, 5$), and, therefore, indirectly contribute to the observed spectrum of the nitrogen afterglow.

The $N_2(^5\Sigma_g^+)$ molecules are in equilibrium with nitrogen atoms under the reaction (1) and reactions (2-6). Therefore, at equilibrium

$$k_1(N)^2(M) = N_2(^5\Sigma_g^+)\ [k_2 + k_3 + k_4 + k_5 + k_6](M)$$

where (M), (N) and $(N_2{}^5\Sigma_g^+)$ are the concentrations of the respective species. In the present case, N_2 molecule acts as a third body, M. The equilibrium concentration of the $N_2{}^5\Sigma_g^+$ molecule is, therefore, given by

$$(N_2{}^5\Sigma_g^+) = \frac{k_1}{k_2 + k_3 + k_4 + k_5 + k_6}(N)^2 \tag{11}$$

The formation of N_2 in $B^3\Pi_g$, $y^3\Sigma_u^-$ and $^3\Delta_u$ states is responsible for the long wavelength end of spectrum of the Lewis-Rayleigh afterglow. Therefore, the observed intensity of emission on the long wavelength end of the spectrum is given by

$$I(vis) = K_1(N_2{}^5\Sigma_g^+)(N_2)(k_3 + k_4 + k_5) \tag{12}$$

where K_1 is a constant which depends on the units, sensitivity and geometry of the photometric system. Substituting the value of $(N_2{}^5\Sigma_g^+)$ from (11) into (12), we have

$$I(vis) = \frac{K_1\ k_1(N)^2\ (N_2)(K_3 + k_4 + k_5)}{k_2 + k_3 + k_4 + k_5 + k_6}, \tag{13}$$

which shows that the intensity of the visible region of the emission from the Lewis-Rayleigh afterglow of nitrogen should be directly proportional to the pressure (N_2) and the square of the nitrogen atom concentration. Rayleigh[12] has shown the linear pressure dependence of the visible emission of the nitrogen afterglow in the 10^{-2} to 10^{-1} mm Hg pressure region and Kash[13] has shown it in the region of pressure between 4 and 50 mm Hg pressure. Berkowitz, et al.[3] have shown that the intensity of the visible radiation is directly proportional to the square of the nitrogen atom concentration.

Proceeding as above, it can be shown that the intensity of the vacuum ultraviolet emission from the Lewis-Rayleigh afterglow of nitrogen is given by

$$I(\mathrm{vuv}) = K_2 \frac{k_1 k_6 (N)^2 \; (N_2)}{k_2 + k_3 + k_4 + k_5 + k_6} \tag{14}$$

where K_2 is a constant which depends on the units, sensitivity and the geometry of the photometric system. According to the above mechanism, the ratio of intensity of visible to that of the vacuum ultraviolet emission from the nitrogen afterglow is given by

$$\frac{I(\mathrm{vis})}{I(\mathrm{vuv})} = \frac{K_1}{K_2} \frac{k_3 + k_4 + k_5}{k_6} \tag{15}$$

and, therefore, should be linearly related. However, it can be seen from Figure 7 that the relationship between I(vis) and I(vuv) is not linear over a wide range of the variation of intensity. This difference may be due to the variation of pressure in the afterglow tube. Therefore, the observed ratio of I(vis)/I(vuv) is plotted against the total pressure in the afterglow tube in Figure 8 which shows that at pressures below about 250 microns,

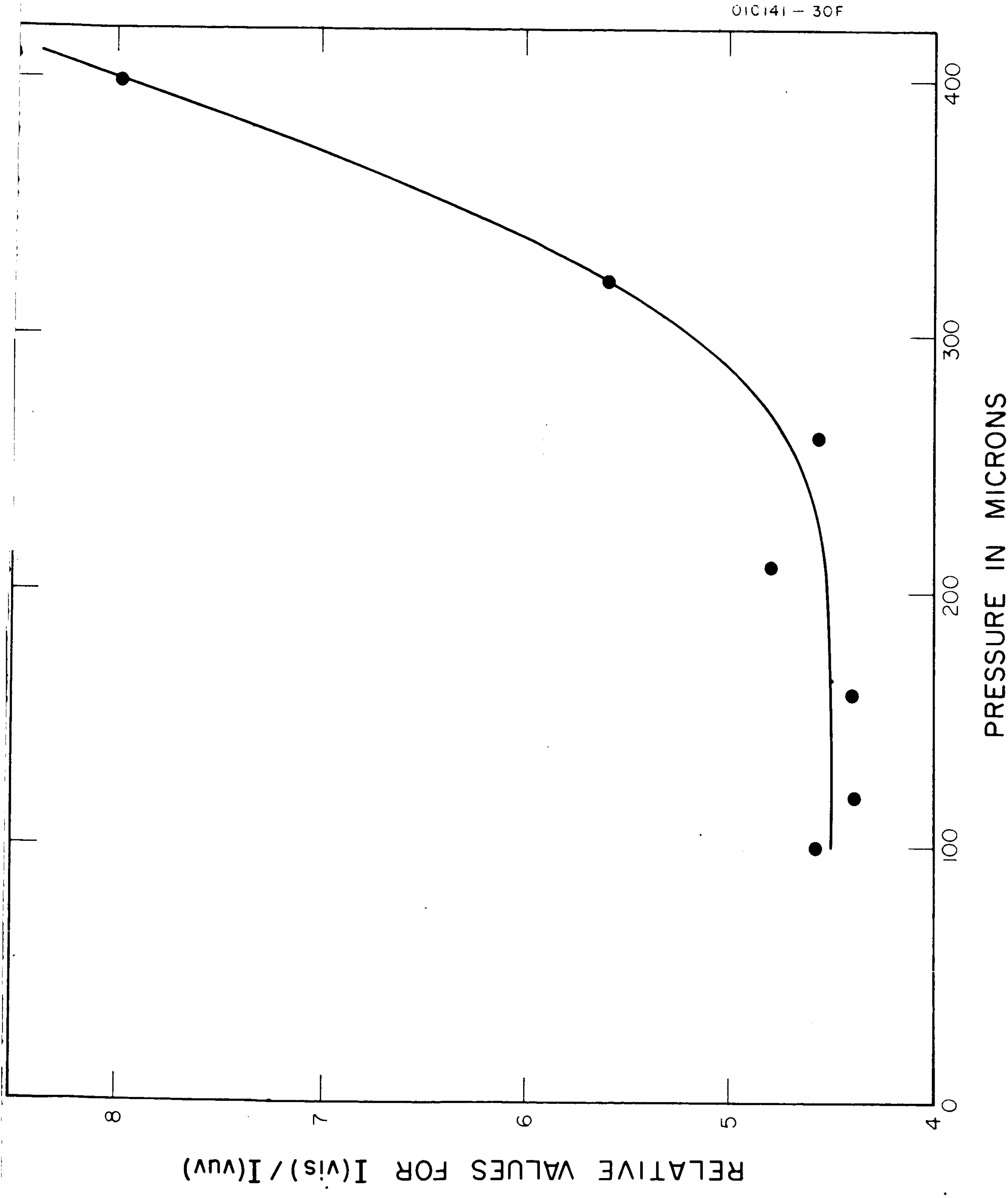

01C141 – 30F
RELATIVE VALUES FOR I(vis)/I(vuv)
PRESSURE IN MICRONS
0
100
200
300
400
4
5
6
7
8

Figure 8.

the ratio of I(vis)/I(vuv) may be constant. However, at higher pressures the ratio increases which indicates that the relative intensity of vacuum ultraviolet radiation is decreased. This can be explained as follows: the upper electronic states ($B^3\Pi_g$, $y^3\Sigma_u^-$, and $^3\Delta_u$) responsible for the emission of visible radiation from the nitrogen afterglow are nonmetastable states with a lifetime of $\leq 10^{-6}$ seconds. On the other hand, the upper electronic state ($a^1\Pi_g$) involved in the vacuum ultraviolet emission of the Lewis-Rayleigh afterglow of nitrogen is a metastable state. Lichtin[14] has found that its lifetime is $(1.7 \pm 0.3) \times 10^{-4}$ sec. Therefore, the $a^1\Pi_g$ state should be more readily quenched than the upper states responsible for the visible emission. Hence, one can incorporate the quenching of $a^1\Pi_g$ state in the above mechanism (1-10) by adding the following process:

$$N_2(a^1\Pi_g) + M \rightarrow N_2' + M \qquad Q_6 \tag{17}$$

where Q_6 is the rate coefficient of the above reaction and M represents an N_2 molecule. The intensity of the vacuum ultraviolet radiation is then given by

$$I(vuv) = K_2 \frac{k_1 k_6 (N)^2 (M)}{k_2 + k_3 + k_4 + k_5 + k_6} \frac{A_6}{A_6 + Q_6(N_2)} \cdot \tag{18}$$

The ratio of the intensity of the visible and vacuum ultraviolet radiation from the afterglow is

$$\frac{I(vis)}{I(vuv)} = \frac{K_1}{K_2} \frac{k_3 + k_4 + k_5}{k_6} \frac{A_6 + Q_6(N_2)}{A_6} \tag{19}$$

which shows that at low pressure where

$$A_6 \gg Q_6(N_2) ,$$

the ratio of the two intensities should be independent of pressure and is given by

$$\left[\frac{I(vis)}{I(vuv)}\right]_o = \frac{K_1}{K_2} \frac{k_3 + k_4 + k_5}{k_6} . \tag{20}$$

However, at higher pressure the ratio I(vis)/I(vuv) should linearly increase with increasing pressures and can be expressed as

$$\left[\frac{I(vis)}{I(vuv)}\right]_p = \left[\frac{I(vis)}{I(vuv)}\right]_o \frac{A_6 + Q_6(N_2)}{A_6} . \tag{21}$$

Substituting in the above equation, we find that the average value of Q_6 is about 2×10^{-13} cm^3/sec which gives a quenching cross section of about 10^{-18} cm^2. The above quenching cross section is considerably less than that for some allowed transitions. Ghosh, et al.[15] have given 1.8×10^{-14} cm^2 for the quenching cross section for the $B^2\Sigma^+$ state of CN by CH_2Cl_2; Carrington[16] gives a value of 3.5×10^{-15} cm^2 for the quenching of the electronic excited OH radical by H_2O. Considering the fact that OH and CN radicals are very reactive, the high quenching cross sections are possible. However, in the present case, since no strong chemical interaction is possible, a low quenching cross section is expected.

D. COLLATERAL INVESTIGATIONS

The technical discussions in this section are reserved for technical areas which have been investigated under the present contract but are considered to be collateral to the major objectives under the Work Statement.

During the current Quarter, two studies have been completed that fall into this category: (1) CO_2 actinometer for argon source and (2) a suggested total eclipse experiment for deriving the deactivation coefficient of the metastable $O^+(^2P)$ ion by observing the decay rate of λλ 7330Å to 7319Å.

1. CO_2 Actinometer for Argon Source

For proper performance of the current program, it became necessary to make quantitative photolysis measurements with a microwave-powered argon light source which emits lines at 1048Å and 1066Å. During the investigation it was learned that no suitable actinometer for this wavelength had been described in the literature. Accordingly, in the present work a nickel photocathode device was constructed and calibrated against an NO-filled ion chamber so that this represented the first actinometer for this light source. With this in hand it then became possible to check the quantum yield for the photolysis of CO_2 at the argon lines. It turned out that, indeed, the CO_2 photolysis was carefully studied for these two lines and a quantum yield of unity was obtained which added some degree of confidence to the original study. These studies were correlated with the CO_2 photolyses experiments at 1470Å and around 1700Å previously performed. Clearly, then, these results can now be employed by any laboratory for actinometry of the argon light source.

No detailed results are given in this section since they are included in a paper which has been submitted for publication in the Journal of the Optical Society of America. The paper is entitled "CO_2 Actinometer for Argon Source" by P. Warneck.

2. <u>A Suggested Total Eclipse Experiment for Deriving the Deactivation Coefficient of the Metastable $O^+(^2P)$ Ion by Observing the Decay Rate of λλ 7330Å to 7319Å</u>

The studies of the dayglow are potentially very valuable sources of information on chemical and ionospheric processes in the atmosphere. Unfortunately, ground observations of relatively low intensity discrete radiations are precluded by the presence of strong scattering owing to the lower earth atmosphere. The possibility of observing these lines is periodically afforded by a total eclipse. During the month of November, 1966, a total eclipse will prevail in South America. Concerning the possibility of performing observations at that time, the following brief comments apply.

Work recently performed under the current contract and reported in GCA Technical Report No. 65-15-N by A. Dalgarno and M. B. McElroy was employed as a background for the following concept for a proposed solar eclipse experiment designed to derive the deactivation coefficient of the metastable $O^+(^2P)$ ion and to gain some insight into the primary excitation mechanism.

The O II doublet in the region of 7320Å is excited by the fluorescence of solar-ionizing radiation according to the process

$$h\nu + O(1s^2 2s^2 2p^4\ {}^3P) \rightarrow e + O^+(1s^2 2s 2p^3\ {}^2P)$$

$$O^+(1s^2 2s^2 2p^3\ {}^2P) \rightarrow O^+(1s^2 2s^2 2p^3\ {}^2D) + \lambda\lambda(7330\text{–}7319\text{Å}).$$

It may be excited, in addition, by corpuscular bombardment if any is occurring. Depending upon altitude and depending upon the rate coefficients, the metastable $O^+(^2P)$ ion may be deactivated before radiating. The most probable mechanism is a collision with molecular nitrogen, say,

$$O^+(^2P) + N_2 \rightarrow NO^+ + N$$

$$O^+(^2P) + N_2 \rightarrow O + N_2^+ .$$

The production rate of $O^+(^2P)$ during the eclipse can be calculated using extensions of programs we have developed for normal daytime. Then, knowledge of the altitude distribution (or equivalently the time variation) clearly yields the deactivation rate coefficient. Note that if the profile cannot be reproduced on the assumption of fluorescence and deactivation, it will provide clear evidence of an additional excitation source. If such a source exists, it is natural to suggest corpuscular bombardment and this can be checked by examining the profile or time variation of the green line and of the N_2^+ radiation.

Clearly, there exists a multitude of lines which would be interesting to observe. However, a survey of proposed experiments has shown that most of these are being considered by others whereas it appears that the above suggestion is new.

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